

anion from the coordination sphere. Alternatively, but less likely, a chelating triflate is involved, and the first step involves a ring-opening reaction.

The aquation kinetics of $\text{trans-M(en)}_2\text{Cl}(\text{OSO}_2\text{CF}_3)^+$, $\text{M} = \text{Rh}$ and Ir , exhibited only one fast aquation step; plots of $\log(A_t - A_\infty)$ vs. time were linear over at least 5 half-lives. This observation is consistent with their formation as chloro triflate complexes, since aquation of coordinated chloride is very slow for these metal centers. In each case, ^{13}C NMR evidence indicated aquation was stereoretentive. The behavior of the Rh and Ir complexes is consistent with the general observation of largely stereoretention during aquation of these complexes in contrast to the cobalt chemistry.⁷³

The synthetic utility of a large range of triflate complexes including osmium and ruthenium polypyridines and osmium pentaammine is presently being explored. They are not only valuable intermediates for the synthesis of mononuclear complexes but are being used extensively in these laboratories and elsewhere for the synthesis of binuclear and polynuclear species for use in studies of mixed-valence complexes and intramolecular electron transfer. Clearly, their potential uses are many-fold and their utility in preparative inorganic chemistry has only just begun to be explored. They also allow comparative studies on the substitution kinetics of a wide range of analogous series of complexes.

(73) *Inorg. React. Mech.* 1-7.

(74) Lay, P. A.; Magnuson, R. H.; Taube, H., to be submitted for publication in *Inorg. Chem.*

Acknowledgment. We thank the Microanalytical Service Unit, The Australian National University, and F. Galsbøl, Ørsted Institute, University of Copenhagen, for an authentic sample of $[\text{Ir}(\text{en})_3]\text{Cl}_3$ and a preliminary account of its synthesis. We are also grateful to Dr. N. J. Curtis for helpful discussions.

Registry No. $[\text{Rh}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 84254-57-9; $[\text{Cr}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 84254-61-5; $[\text{Ir}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 84254-59-1; $[\text{Ru}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 84278-98-8; $[\text{Pt}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_3$, 84254-63-7; $[\text{Cr}(\text{N}(\text{H}_2\text{CH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 90065-87-5; $[\text{Co}(\text{NH}_2\text{CH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 90065-88-6; $[\text{Rh}(\text{NH}_2\text{CH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)_2$, 90065-89-7; *cis*- $[\text{Cr}(\text{en})_2(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)$, 90065-91-1; *cis*- $[\text{Rh}(\text{en})_2(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)$, 90065-93-3; *cis*- $[\text{Ir}(\text{en})_2(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)$, 90065-95-5; *trans*- $[\text{Rh}(\text{en})_2\text{Cl}(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)$, 90065-97-7; *trans*- $[\text{Ir}(\text{en})_2\text{Cl}(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)$, 90065-99-9; *cis*- $[\text{Co}(\text{en})_2(\text{OSO}_2\text{CF}_3)](\text{CF}_3\text{SO}_3)$, 75522-52-0; $[\text{Cr}(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$, 32700-25-7; $[\text{Cr}(\text{NH}_3)_5(\text{NCC-H}_3)](\text{CF}_3\text{SO}_3)_3$, 90066-01-6; $[\text{Cr}(\text{NH}_3)_5(\text{OC}(\text{NH}_2)_2)](\text{S}_2\text{O}_8)_3^{2-}$, 87564-83-8; $[\text{Rh}(\text{NH}_3)_5(\text{OH}_2)](\text{ClO}_4)_3$, 15611-81-1; $[\text{Rh}(\text{NH}_3)_6](\text{CF}_3\text{SO}_3)_3$, 90084-45-0; $[\text{Ir}(\text{NH}_3)_5(\text{OH}_2)](\text{CF}_3\text{SO}_3)_3$, 90084-46-1; $[\text{Ru}(\text{NH}_3)_5(\text{HOCH}_3)](\text{CF}_3\text{SO}_3)_3$, 90066-03-8; $[\text{Ir}(\text{NH}_3)_6](\text{CF}_3\text{SO}_3)_3$, 90066-04-9; *cis*- $[\text{Rh}(\text{en})_2(\text{NH}_3)](\text{CF}_3\text{SO}_3)_3$, 90066-05-0; *trans*- $[\text{Rh}(\text{en})_2(\text{NH}_3)\text{Cl}](\text{CF}_3\text{SO}_3)_2$, 90130-09-9; $[\text{Rh}(\text{en})_3]\text{Cl}_3$, 14023-02-0; $[\text{Ir}(\text{en})_3]\text{Cl}_3$, 29031-66-1; $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, 13820-95-6; $[\text{Cr}(\text{N}(\text{H}_3)_5\text{Cl})\text{Cl}_2$, 13820-89-8; $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, 15742-38-8; $[\text{Ru}(\text{N}(\text{H}_3)_5\text{Cl})\text{Cl}_2$, 18532-87-1; $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$, 16893-11-1; $[\text{Cr}(\text{NH}_2\text{C}(\text{H}_3)_5\text{Cl})\text{Cl}_2$, 15351-84-5; $[\text{Co}(\text{NH}_2\text{CH}_3)_5\text{Cl}]\text{Cl}_2$, 15392-59-3; $[\text{Rh}(\text{NH}_2\text{CH}_3)_5\text{Cl}]\text{Cl}_2$, 64459-98-9; *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$, 14240-29-0; *cis*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$, 15444-62-9; *cis*- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$, 15444-47-0; *trans*- $[\text{Rh}(\text{en})_2\text{Cl}_2]\text{Cl}$, 15444-63-0; *trans*- $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{Cl}$, 15444-46-9.

Contribution from CNR-Centro di studio per la sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione, Via G. Venezian 21, 20133 Milano, Italy, Dipartimento di Chimica Inorganica e Metallorganica, Università di Milano, Via G. Venezian 21, 20133 Milano, Italy, and Chemical Laboratory, University of Kent, Canterbury CT2 7NH, England

Mixed Pt-Rh Carbonyl Clusters. 1. Synthesis, Reactivity, and Solution Structures of $[\text{PtRh}_5(\text{CO})_{15}]^-$, $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$, and $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$

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Received October 13, 1983

The reductive carbonylations of mixtures of Na_2PtCl_6 and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (at room temperature and 1 atm CO) are reported. From the reaction mixtures $[\text{PtRh}_5(\text{CO})_{15}]^-$ and $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ have been isolated; the latter is in equilibrium, through the release and absorption of CO, with $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$. Solution structures and fluxional behavior of all these anions have been established by multinuclear (^{13}C , $^{13}\text{C}\{^{103}\text{Rh}\}$, ^{103}Rh , ^{195}Pt) variable-temperature NMR measurements.

Introduction

We reported, in a preliminary communication,² the isolation of $[\text{PtRh}_5(\text{CO})_{15}]^-$, which reacted further under CO with an alkaline methanolic solution or Na-anthracene in THF to give an orange-yellow anion. This was formulated on the basis of partial analytical data to be $[\text{PtRh}_2(\text{CO})_x]^{n-}$, which we now show to be $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$. This reversibly loses CO to give the related dianion $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$. The general features of the reductive carbonylation of mixtures containing Na_2PtCl_6 and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ are discussed in connection with the preparation of the above clusters. Multinuclear NMR studies (^{13}C , $^{13}\text{C}\{^{103}\text{Rh}\}$, ^{103}Rh , and ^{195}Pt) are reported which establish their structures and fluxional behavior in solution.

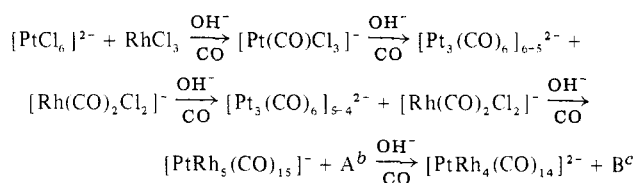
Results and Discussion

1. Generalities on the Reductive Carbonylation of Pt-Rh Systems. In an attempt to develop synthetic routes to mixed Pt-Rh clusters in good yields from readily available materials, we have carried out a systematic investigation of the reductive carbonylation of mixtures of Na_2PtCl_6 and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ in methanol under CO (1 atm pressure) at room temperature. The reduction was carried out by a stepwise addition of NaOH (1 M in methanol) to a vigorously stirred solution with various ratios of Pt:Rh (1:1, 1:2, 1:4, 1:5) under an atmosphere of CO; the reactions were monitored by IR after each addition of NaOH or at regular intervals. When an unambiguous interpretation of the spectra was not possible, excess bulky cations were added to precipitate the equilibrium mixture, which was then subjected to fractional crystallization. In every case, the same species were always formed first, though in different proportions. The final distribution of products, however, depends on both the ratios of OH^- :metals and Pt:Rh;

(1) (a) CNR. (b) Università di Milano. (c) University of Kent. (d) Deceased.

(2) Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Brückner, S.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* 1978, 195.

Scheme I. Carbonyl Species Observed in the Stepwise Reductive Carbonylation of $[\text{PtCl}_6]^{2-}$ and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}^a$



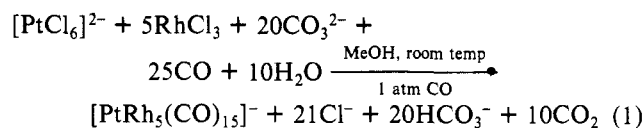
^a Performed in methanol at room temperature under 1 atm CO with stepwise addition of NaOH. ^b Byproducts A: $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$ if Pt:Rh < 1:5; $[\text{Pt}_3(\text{CO})_6]_{4-3}^{2-}$ if Pt:Rh > 1:5. ^c Byproducts B: $[\text{Rh}_6(\text{CO})_{16}]^{2-}$ and $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ if Pt:Rh < 1:4; $[\text{Pt}_3(\text{CO})_6]_{3-2}^{2-}$ if Pt:Rh > 1:4.

the first determines the type of mixed species present at the end of the reaction (viz. $[\text{PtRh}_5(\text{CO})_{15}]^-$ is stable only in well-controlled basicity conditions, whereas $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ is stable in excess OH^-) and the Pt:Rh ratio, at a given ratio of OH^- :metals, determines the relative amounts of product and byproducts. It has to be noted that after each addition of base the above equilibria are established surprisingly quickly (10–15 min) when compared to the similar reduction of Na_2PtCl_6 only,³ and this suggests a catalytic effect by Rh on the reduction of Pt.

As shown in Scheme I, the only carbonyl species detectable by IR at the beginning of the reduction is $[\text{Pt}(\text{CO})\text{Cl}_3]^-$, and it is only upon further addition of NaOH, when the solution turns from yellow-red to green-yellow and becomes cloudy because of precipitation of NaCl, that the first rhodium carbonyl species, $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$, is observed along with trace amounts of $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 6, 5$).³ Deep green and then blue-green solutions, consistent with the presence of $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 5, 4$), are formed on further addition of NaOH, but $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ is still present; at this stage the first mixed species, $[\text{PtRh}_5(\text{CO})_{15}]^-$, is observed in the IR spectra, together with $[\text{Pt}_3(\text{CO})_6]_{4-3}^{2-}$ and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ while the solution slowly turns brown. By careful addition of more NaOH (OH^- :Pt = ca. 20) at a Pt:Rh ratio of 1:5 the brown hexanuclear anion $[\text{PtRh}_5(\text{CO})_{15}]^-$ can be obtained almost pure; with Pt:Rh ratios other than 1:5 the byproducts are essentially $[\text{Pt}_3(\text{CO})_6]_{4-3}^{2-}$ or $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ and $[\text{Rh}_5(\text{CO})_{15}]^-$,⁵ respectively, depending on the metal present in excess. Addition of a slight excess of base over that required for formation of $[\text{PtRh}_5(\text{CO})_{15}]^-$ results in the rapid disappearance of the above clusters and formation of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$. When the ratio of Pt:Rh is exactly 1:4, this anion is obtained in a nearly pure form whereas if this ratio is only slightly different the solution appears red or greenish due to the presence of $[\text{Pt}_3(\text{CO})_6]_{3-2}^{2-}$ or $[\text{Rh}_6(\text{CO})_{15}]^{2-}$ and $[\text{Rh}_7(\text{CO})_{16}]^{3-}$,⁶ respectively. This situation remains unchanged upon further addition of NaOH up to the 1 M concentration.

2. Synthesis and Reactivity of $[\text{PtRh}_5(\text{CO})_{15}]^-$. The best way to obtain high yields of $[\text{PtRh}_5(\text{CO})_{15}]^-$ on a large scale is by the reductive carbonylation of a mixture of Na_2PtCl_6 and $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ in the molar ratio 1:5, according to the general synthetic procedure described above. To avoid such a laborious procedure, we have searched for slightly basic buffered systems, employing calculated amounts of (a) CH_3COONa , (b) NaHCO_3 , or (c) Na_2CO_3 instead of sodium hydroxide. All three methods proved effective but with some limitations: Method a is rather slow (it takes about 1 week to go to completion) because of formation of stable Rh-acetate complexes which undergo reduction very slowly. Method b also proceeds

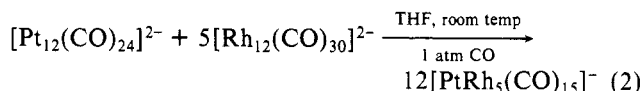
slowly (2–3 days) because of the immediate formation of a buffer, $\text{CO}_2/\text{HCO}_3^-$, which significantly slows the reductive process. Method c provides a high-yield synthesis in a reasonable time (12–18 h) but has to be performed in such a way that the evolved CO_2 does not escape; this gives, but only near the end of the reaction, the above mentioned $\text{CO}_2/\text{HCO}_3^-$ buffer in which the mixed-metal cluster is stable. The formal stoichiometry of this reaction is



The product can be obtained directly as the sodium salt or, by metathesis, as a bulky cation salt, in yields up to 80–85%.

Solutions of $[\text{PtRh}_5(\text{CO})_{15}]^-$ (THF, CH_2Cl_2 , acetone) at room temperature are decomposed within minutes in air, but the solid is somewhat more stable, especially the large crystals of the $[\text{PPN}]^+$ salt, which can be obtained by slow diffusion of pentane into THF solutions.

We have previously reported² that the dodecanuclear species of Pt³ and Rh⁴ react according to eq 2. Because it requires



previous preparation of both reactants, this reaction is of little synthetic interest but it is important in understanding the peculiar reactivity of the mixed anion toward CO. It has been observed that the reaction does not proceed under a nitrogen atmosphere, while there is a slow reaction (ca. 12 h) under CO. With $[\text{N}-n\text{-Bu}_4]^+$ or $[\text{PPN}]^+$ as counterions, $[\text{PtRh}_5(\text{CO})_{15}]^-$ seems to be the only product present and indefinitely stable under these conditions. However, a THF solution of $(\text{M})[\text{PtRh}_5(\text{CO})_{15}]$ ($\text{M} = \text{Na}$ or $[\text{NEt}_4]^+$) under 1 atm CO undergoes slow precipitation of $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$,⁴ which is rather insoluble in THF as a salt of these cations. This suggests that reaction 2 is reversible and should be regarded as an equilibrium. The situation is, however, more complicated because under CO $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ is known to be in equilibrium with $[\text{Rh}_5(\text{CO})_{15}]^-$,⁵ which is thus very probably involved as an intermediate in eq 2, and this would explain the lack of reaction under N_2 . Further evidence for the involvement of $[\text{Rh}_5(\text{CO})_{15}]^-$ in the formation and degradation of $[\text{PtRh}_5(\text{CO})_{15}]^-$ comes from the reaction of this mixed anion under a slightly higher pressure of CO (3–5 atm); the original brown solution becomes grayish and the IR spectrum shows the presence of mainly $[\text{Rh}_5(\text{CO})_{15}]^-$ along with perhaps $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 4-5$). This mixture reverts back to $[\text{PtRh}_5(\text{CO})_{15}]^-$ within a few hours if the CO pressure is released to 1 atm. The similar behavior toward CO of the analogous species $[\text{NiRh}_5(\text{CO})_{15}]^-$ ⁸ should be noted, since this also gives $[\text{Rh}_5(\text{CO})_{15}]^-$ along with $\text{Ni}(\text{CO})_4$.

Thermogravimetric measurements on solid $(\text{M})[\text{PtRh}_5(\text{CO})_{15}]$ ($\text{M} = [\text{PPN}]^+$ or $[\text{NEt}_4]^+$) indicate a two-step decomposition. The first, which starts between 120 and 140 °C and ends at about 200 °C (depending upon the cation and the N_2 or CO atmosphere), is consistent with loss of about 4–5 mol of CO/mol of compound; subsequently, a further progressive loss occurs in the range 250–400 °C, leaving an essentially, but not entirely, metallic residue. The product obtained in the first step has been found to be a complex mixture of presently unidentified species, which are very likely high-nuclearity clusters. A similar result is obtained when solutions of $[\text{PtRh}_5(\text{CO})_{15}]^-$ are heated, under both N_2 and CO; mix-

(3) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225.

(4) Chini, P.; Martinengo, S. *Inorg. Chim. Acta* **1969**, *3*, 299.

(5) Fumagalli, A.; Koetzle, T. F.; Takusagawa, F.; Chini, P.; Martinengo, S.; Heaton, B. T. *J. Am. Chem. Soc.* **1980**, *102*, 1740.

(6) Martinengo, S.; Chini, P. *Gazz. Chim. Ital.* **1972**, *102*, 344.

(7) $[\text{PPN}]^+$ = bis(triphenylphosphine)nitrogen(1+) cation.

(8) Fumagalli, A.; Longoni, G.; Chini, P.; Albinati, A.; Brückner, S. *J. Organomet. Chem.* **1980**, *202*, 329.

Table I. IR Data

compd	cation	solvent ^a	$\nu(\text{CO}), \pm 5 \text{ cm}^{-1} \text{ }^b$
[PtRh ₅ (CO) ₁₅] ⁻	Na	a	2060 vw, 2030 s, 2005 m, 1790 ms
	Na	b	2077 vw, 2035 s, 2004 m, 1785 ms
	NEt ₄	b	2080 vw, 2038 s, 2005 m, 1785 ms
	PPN	b	2078 vw, 2034 s, 2004 m, 1785 ms
[PtRh ₄ (CO) ₁₄] ²⁻	Na	a	2006 s, 1973 s, 1813 m, 1775 m
	PPN	b	2030 w, 1995 s, 1962 s, 1941 sh, 1854 vw, 1807 m, 1800 m, 1750 m
	N- <i>n</i> -Bu ₄	b	2025 w, 1995 s, 1955 s, 1855 mw, 1810 ms, 1785 m, 1735 mw
	NEt ₃ - <i>n</i> -Pr	c	2025 w, 1995 s, 1960 s, 1808 ms, 1795 m, 1740 mw
	PPh ₄	b	2015 w, 1993 s, 1955 s, 1800 ms, 1745 mw
	PPh ₄	d	2015 w, 2000 s, 1965 s, 1800 ms, 1745 mw
[PtRh ₄ (CO) ₁₂] ²⁻	N- <i>n</i> -Bu ₄	b	2010 w, 1988 s, 1953 s, 1860 w, 1815 ms, 1800 ms, 1770 sh
	PPN	b	2015 w, 1982 s, 1947 s, 1859 w, 1812 ms, 1788 m

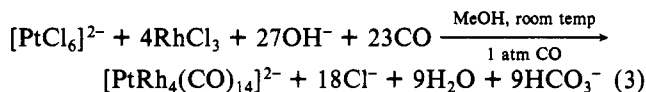
^a Legend: (a) MeOH; (b) THF; (c) dimethoxyethane; (d) MeCN. ^b Abbreviations: vw, very weak; w, weak; m, medium; s, strong; sh, shoulder.

tures of brown anions are obtained, and their identification is still in progress.

The reaction of an aqueous solution of Na[PtRh₅(CO)₁₅] with slight excess of aqueous HCl gives precipitation of a product that we believe to be [HPtRh₅(CO)₁₅]. Unfortunately, both its poor stability and solubility prevented us from obtaining a ¹H NMR spectrum. This formulation, however, is supported by the IR spectrum in CH₂Cl₂, which has bands at 2065 s, 2035 m, and 1810 ms cm⁻¹. Both the shift to higher wavenumbers (20–30 cm⁻¹) and the pattern, almost identical with that of the parent compound, are in keeping with the existence of such hydridic species.

Attempts to obtain neutral species by controlled oxidation with FeCl₃, Ag₂SO₄, AgBF₄, or I₂, in THF under N₂ or CO, gave mixtures that contained [Rh₆(CO)₁₆], [Pt₃(CO)₆]_{*n*}²⁻ (*n* ≥ 6),³ and [Pt(CO)I₃]⁻ along with unidentified products.

3. Synthesis of [PtRh₄(CO)₁₄]²⁻. This synthesis is accomplished by stirring under CO a methanolic solution of Na₂PtCl₆ and RhCl₃·*x*H₂O in a 1:4 molar ratio treated with a slight excess of the stoichiometric amount of NaOH according to eq 3. The reaction is monitored by IR and is complete within



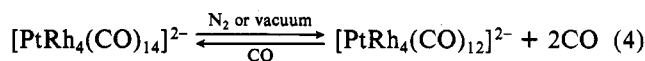
12–18 h, when the characteristic bands of the anion at 2005, 1973, 1815, and 1775 cm⁻¹ are present and a yellow-orange cloudy solution is formed. It is essential that the correct ratio of metals is used in order to avoid formation of byproducts and subsequent separation problems. However, we noted that, even on starting from the correct ratio of metals, sometimes part of the Pt or Rh precipitates from the reaction mixture as an unreactive insoluble product (not yet characterized), thereby changing the initial Pt:Rh ratio in solution. When this happens, it is possible to retrieve the correct metal ratio by adding small amounts of Na₂PtCl₆ or RhCl₃·*x*H₂O, whichever is required, and allowing the reaction to proceed; IR monitoring shows that the equilibrium is quickly reestablished.

The determination of the minimum amount of NaOH required to reach a complete conversion to [PtRh₄(CO)₁₄]²⁻ is consistent with the stoichiometry shown in eq 3. However, it should be noted that a slight excess of NaOH is not detrimental.

All the salts of [PtRh₄(CO)₁₄]²⁻ must be handled and stored under a CO atmosphere; they are soluble in acetone, THF, and acetonitrile but insoluble in 2-propanol and are air sensitive both in solution and in the solid state.

4. Synthesis of [PtRh₄(CO)₁₂]²⁻. The orange-yellow dianion [PtRh₄(CO)₁₄]²⁻ is unstable under nitrogen, both in solution and in the solid state, due to ready loss of carbon monoxide causing the color to change to reddish brown. This process

is fast under vacuum, and a few cycles of evacuation to dryness followed by redissolution in THF or acetone results in complete conversion to the related species [PtRh₄(CO)₁₂]²⁻ (eq 4). The

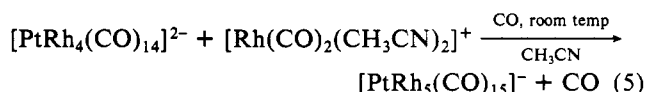


stoichiometry of the reaction has been confirmed by gas-volumetric measurements (see Experimental Section). The CO evolution results in a shift of the IR absorptions to lower wavenumbers that is particularly evident in the terminal-CO region (a decrease of 5–15 cm⁻¹ depending on the counter-cation; see Table I). This is consistent with the loss of ligands and consequent increased back-donation toward the remaining CO's.

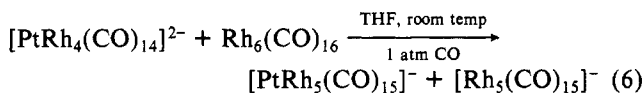
The brown-red [PtRh₄(CO)₁₂]²⁻ dianion has been crystallized as [N-*n*-Bu₄]⁺ and [PPN]⁺ salts from acetone or THF solution by slow diffusion of 2-propanol under nitrogen. All the salts, obtained with a variety of cations, are soluble in acetone and acetonitrile, moderately soluble in THF (but less than those of the parent [PtRh₄(CO)₁₄]²⁻ anion), and insoluble in 2-propanol. They are sensitive to air, which causes decomposition, in both the solid and solution, to as yet uncharacterized brown species.

5. Reactivity of [PtRh₄(CO)_{*n*}]²⁻ (*n* = 12 and 14). The behavior of these two species with respect to carbon monoxide is rather interesting. In fact, through the absorption and release of CO, the two clusters appear to be in reversible equilibrium (eq 4). At room temperature and 1 atm CO there is IR evidence only of the species at the left, and in fact only this one is recovered by precipitation under these conditions, although we cannot exclude the presence of trace amounts of [PtRh₄(CO)₁₂]²⁻ in solution. However, under a nitrogen atmosphere or vacuum, complete conversion to [PtRh₄(CO)₁₂]²⁻ occurs and these reactions may be continuously recycled.

The reactivity of both anions was also studied in order to synthesize other mixed clusters and to understand the equilibria between heteronuclear and homonuclear species. One particular type of reaction, designed to build up larger clusters by means of condensation of small fragments, was tried. Thus, both [PtRh₄(CO)₁₄]²⁻ and [PtRh₄(CO)₁₂]²⁻ react with the cationic species [Rh(CO)₂(CH₃CN)₂]⁺ to give [PtRh₅(CO)₁₅]⁻ when the reaction is carried out under CO (eq 5), whereas under nitrogen significant amounts of unknown side products are formed together with the hexanuclear mixed cluster.



[PtRh₅(CO)₁₅]⁻ can also be obtained by reacting the mixed pentanuclear clusters with Rh₆(CO)₁₆ under CO. The reaction takes a few hours due to the limited solubility of the neutral carbonyl in THF but seems to proceed according to eq 6. This



reaction is particularly interesting in that there is a redistribution of both metal atoms and charge between clusters.

Reaction with electrophilic agents such as Ag^+ and mineral acids (H_2SO_4 , H_3PO_4) resulted in oxidation to mixtures of brown, as yet uncharacterized products.

Further reduction of the two anions is difficult and under severe conditions (i.e. with KOH in dimethyl sulfoxide) leads, under a CO atmosphere, to disruption of the clusters with formation of $[\text{Rh}(\text{CO})_4]^-$, $[\text{Pt}_3(\text{CO})_6]_2^{2-}$, and perhaps $[\text{Pt}_3(\text{CO})_6]_2^{2-}$.

Attempts to obtain higher nuclearity species by thermal treatment in CH_3CN solution gave, after prolonged reflux under nitrogen, mixtures of dark brown anions, which are under investigation.

6. IR Spectra. Reference IR spectra of all the anions as PPN salts in THF solution are reported in Figure 1. Frequencies in the CO region of a variety of salts are tabulated in Table I. IR spectra of $[\text{PtRh}_5(\text{CO})_{15}]^-$ are negligibly affected on changing the cation and the solvent; the shape and position of the bands are very similar to those found in the series $[\text{Rh}_6(\text{CO})_{15}\text{X}]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}, \text{CN}$),⁹ which are closely related structurally (vide infra). In contrast, the two pentanuclear clusters show, particularly in the bridging carbonyl region, a remarkable dependence upon the cation and/or the solvent, probably because of ion-pairing effects. The IR spectra of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ were recorded under CO, while all the other species were under N_2 .

7. Multinuclear NMR Studies. (a) $[\text{PtRh}_5(\text{CO})_{15}]^-$. The structure of this cluster (Figure 2)² is related to that of $[\text{Rh}_6(\text{CO})_{16}]^{10}$ by replacing a $\text{Rh}(\text{CO})_2$ group with a $\text{Pt}(\text{CO})$ group. The ^{13}C NMR spectrum at -90°C (Figure 3) is completely consistent with this structure and, except for our inability to distinguish between the two well-resolved doublets at 189.8 and 188.4 ppm due to $\text{C}^{\text{b}}\text{O}$ and $\text{C}^{\text{c}}\text{O}$, has been unambiguously assigned by $^{13}\text{C}\{^{100}\text{Rh}\}$ measurements; the data are summarized in Table II.

At -50°C (Figure 3), partial fluxionality occurs as evidenced by the collapse of the resonances due to $\text{C}^{\text{b}}\text{O}$, $\text{C}^{\text{c}}\text{O}$, and $\text{C}^{\text{d}}\text{O}$ with all the other resonances remaining essentially unchanged (Table II). It is not easy to envisage this migratory motion, but at room temperature all the carbonyls clearly become involved in exchange as shown by the presence of a broad resonance at about 198 ppm ($\delta(\text{CO})_{\text{mean}} = 201.3$), which also exhibits satellites due to $J(^{195}\text{Pt}-\text{CO})$, ca. 600 Hz. However, the ^{195}Pt NMR spectrum clearly shows the metal skeleton is intact since a doublet of quintets is observed at +36.2 ppm;¹¹ $^1J(\text{Rh}^{\text{A}}-\text{Pt}) = 24$ Hz, and $^2J(\text{Rh}^{\text{B}}-\text{Pt}) = 73$ Hz. It should be noted that $|^1J(^{195}\text{Pt}-\text{Rh}^{\text{A}})| < ^2J(^{195}\text{Pt}-\text{Rh}^{\text{B}})$, which may arise from a change in sign or, if the one- and two-bond coupling constants have the same sign, from the greater number of pathways for transmission of coupling in the two-bond case.

(b) $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$. The structure of this anion is shown schematically in Figure 4.¹² It is closely related to the solid-state structure of $[\text{Rh}_5(\text{CO})_{15}]^-$ ⁵ with a $\text{Pt}(\text{CO})$ group replacing the unique $\text{Rh}(\text{CO})_2$ group in the equatorial plane. Consistent with this structure, which has a C_2 axis incorpo-

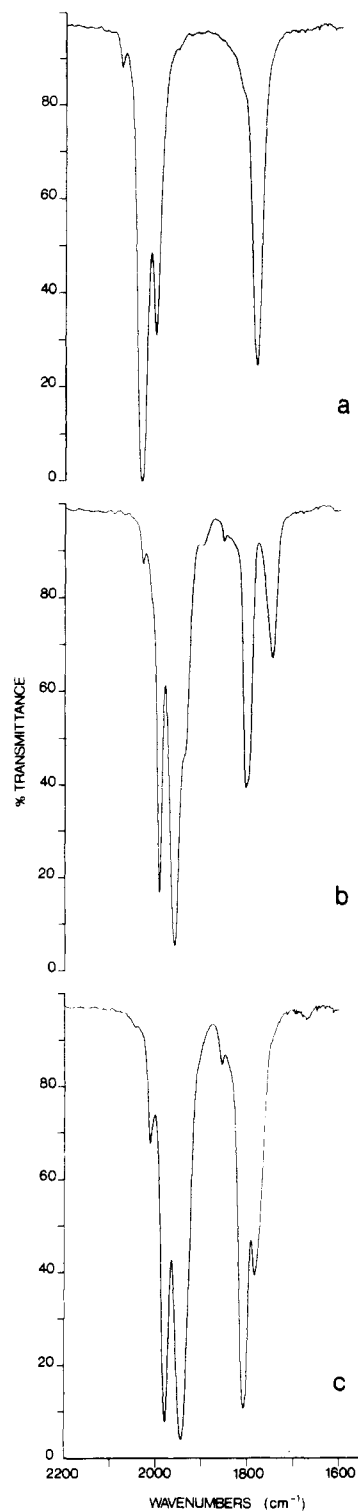


Figure 1. FT IR spectra, ca. 0.01 M in THF with solvent subtraction, of the PPN salts of (a) $[\text{PtRh}_5(\text{CO})_{15}]^-$, (b) $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$, and (c) $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$. Frequencies are listed in Table I.

rating the Pt and the center of the $\text{Rh}_{\text{eq}}-\text{Rh}_{\text{eq}}$ edge, $^{13}\text{C}\{^{103}\text{Rh}\}$ NMR measurements at -105°C show the presence of two rhodium resonances at -297 and -1072 ppm,¹³ which can be unambiguously assigned to Rh_{eq} and Rh_{aq} , respectively, by consideration of the carbonyl resonances (Figure 5). C^1O occurs at highest field (193.2 ppm) and shows characteristic ^{195}Pt satellites ($^1J(\text{Pt}-\text{C}^1\text{O}) = 2250$ Hz). For the other carbonyls attached to Rh_{eq} , C^3O is readily identified since it occurs

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(11) 21.4 MHz = 0 ppm at such a magnetic field that the protons in Me_4Si resonate at exactly 100 MHz.

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(13) 3.16 MHz = 0 ppm at such a magnetic field that the protons in Me_4Si resonate at exactly 100 MHz.

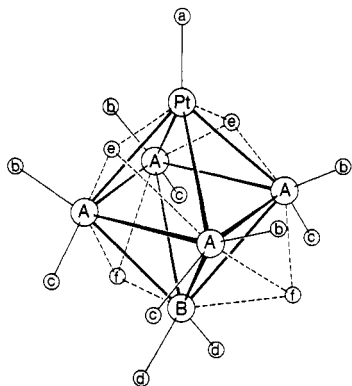


Figure 2. Schematic representation of the structure of $[\text{PtRh}_5(\text{CO})_{15}]^-$.

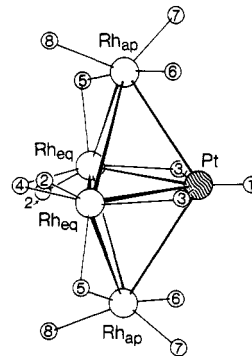


Figure 4. Schematic representation of the structure of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$.

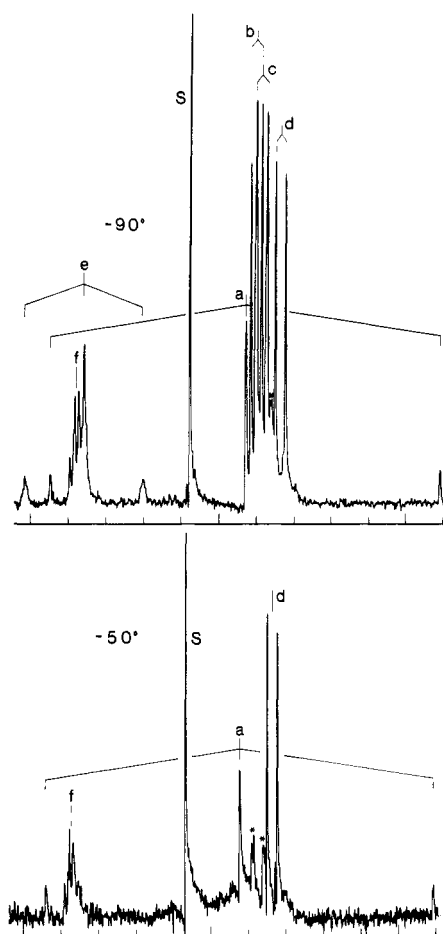


Figure 3. Variable-temperature ^{13}C NMR spectra of $[\text{NET}_4]\text{-}[\text{PtRh}_5(\text{CO})_{15}]$ in acetone- d_6 at -90 and -50 °C. Assignments b and c may be interchanged. The two small doublets marked by asterisks at 187.5 and 186.9 ppm ($J = 80.1$ and 78.6 Hz, respectively) are due to $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ present as an impurity.

as a doublet with associated ^{195}Pt satellites ($\delta(\text{C}^3\text{O}) = 245.5$, $^1J(\text{Rh}_{\text{eq}}-\text{C}^3\text{O}) = 34.4$ Hz, $^1J(\text{Pt}-\text{C}^3\text{O}) = 654$ Hz); C^4O occurs as a triplet ($\delta(\text{C}^4\text{O}) = 256.6$, $^1J(\text{Rh}_{\text{eq}}-\text{C}^4\text{O}) = 31.7$ Hz), and C^5O appears as a doublet of doublets ($\delta(\text{C}^5\text{O}) = 247.4$, $^1J(\text{Rh}_{\text{eq}}-\text{C}^5\text{O}) = 37.1$ Hz, $^1J(\text{Rh}_{\text{ap}}-\text{C}^5\text{O}) = 25.8$ Hz). These assignments have been unambiguously confirmed by specifically decoupling Rh_{eq} , which also allowed C^2O to be assigned ($\delta(\text{C}^2\text{O}) = 205.9$, $^1J(\text{Rh}_{\text{eq}}-\text{C}^2\text{O}) = 93.4$ Hz). Similarly, decoupling Rh_{ap} confirmed the assignment of C^6O , C^7O , and C^8O ($\delta(\text{C}^6\text{O}) = 207.7$, $^1J(\text{Rh}_{\text{ap}}-\text{C}^6\text{O}) = 73.6$ Hz; $\delta(\text{C}^7\text{O}) = 199.9$, $^1J(\text{Rh}_{\text{ap}}-\text{C}^7\text{O}) = 76.2$ Hz; $\delta(\text{C}^8\text{O}) = 197.5$, $^1J(\text{Rh}_{\text{ap}}-\text{C}^8\text{O}) = 79.5$ Hz), but they could not be distinguished.

The variable-temperature ^{13}C NMR spectra of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ (Figure 5) are interesting and clearly show that at

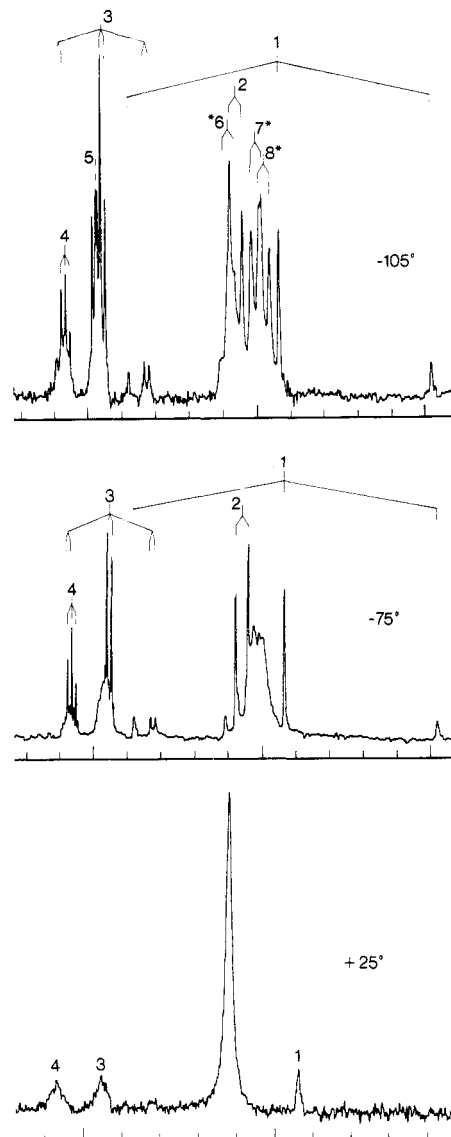


Figure 5. Variable-temperature ^{13}C NMR spectra of $[\text{N-}n\text{-Bu}_4]_2\text{-}[\text{PtRh}_4(\text{CO})_{14}]$ in THF- d_8 at -105 , -75 , and $+25$ °C. Assignments marked by asterisks may be interchanged.

-75 °C there is a rocking motion of the carbonyls on the upper and lower halves of the trigonal-bipyramidal metallic skeleton as was proposed for $[\text{Rh}_5(\text{CO})_{15}]^-$; there is clearly no exchange of $\text{C}^1\text{O}-\text{C}^4\text{O}$. At room temperature, all the carbonyls except C^1O , C^3O , and C^4O are involved in exchange and give a broad resonance at 211.7 ppm exactly in the calculated position (Figure 5, 25 °C). The same nonfluxionality of edge-bridging carbonyls in the Rh_3 equatorial plane was also found in $[\text{Rh}_5(\text{CO})_{15}]^-$ and probably stems from them being coplanar

Table II. NMR Data for $[\text{NEt}_4][\text{PtRh}_5(\text{CO})_{15}]$ in Acetone- d_6 (See Figures 2 and 3)^a

	-90 °C		-50 °C	
	δ	J/Hz	δ	J/Hz
C ^a O	192.5 s + d	2629 (¹ J(Pt-C ^a O))	192.2 s + d	2613 (¹ J(Pt-C ^a O))
C ^b O	189.8 d	71.4 (¹ J(Rh ^A -C ^b O))
C ^c O	188.4 d	74.2 (¹ J(Rh ^A -C ^c O))
C ^d O	183.3 d	69.5 (¹ J(Rh ^B -C ^d O))	183.4 d	69.1 (¹ J(Rh ^B -C ^d O))
C ^e O	235.8 s + d, t	791.2 (¹ J(Pt-C ^e O))
		ca. 14 (¹ J(Rh ^A -C ^e O))
C ^f O	237.7 t, d	32.8 (¹ J(Rh ^A -C ^f O))	237.2 t, d	32.2 (¹ J(Rh ^A -C ^f O))
		24.7 (¹ J(Rh ^B -C ^f O))		24.3 (¹ J(Rh ^B -C ^f O))
		δ^b		J/Hz
Pt		+36.2 q, d	24 (¹ J(Pt-Rh ^A))	73 (² J(Pt-Rh ^B))
Rh ^A		-243.0		
Rh ^B		-495.0		

^a Abbreviations: s, singlet; d, doublet; t, triplet; q, quintet. ^b At 25 °C.

Table III. NMR Data for $[\text{N-}i\text{-Bu}_4]_2[\text{PtRh}_4(\text{CO})_{12}]$ in THF- d_8 (See Figure 6) at -98 °C for ¹³C and ¹⁹⁵Pt Data and at -90 °C for ¹⁰³Rh Data^a

	δ	J/Hz
C ¹ O	189.0 s + d	2425 (¹ J(Pt-C ¹ O))
C ² O	205.6 d	93 (¹ J(Rh ² -C ² O))
C ³ O	197.7 d	90 (¹ J(Rh ¹ -C ³ O))
C ⁴ O	190.4 d	87 (¹ J(Rh ³ -C ⁴ O))
C ^{4'} O	218.7 d	61 (¹ J(Rh ³ -C ^{4'} O))
C ⁵ O	252.2 d, d	31 (¹ J(Rh ¹ -C ⁵ O))
		31 (¹ J(Rh ² -C ⁵ O))
C ⁶ O	247.4 t	26 (¹ J(Rh ² -C ⁶ O))
C ⁷ O	245.5 s + d, d	38 (¹ J(Rh ² -C ⁷ O))
		724 (¹ J(Pt-C ⁷ O))
C ⁸ O	252.9 d, d	35 (¹ J(Rh ¹ -C ⁸ O))
		35 (¹ J(Rh ³ -C ⁸ O))
Pt	+386.9 br	
Rh ¹	+232.7 s + d	44 (¹ J(Pt-Rh ¹))
Rh ²	-475.0 s	
Rh ³	-432.1 s	

^a Abbreviations: s, singlet; d, doublet; t, triplet; br, broad.

with the Rh₂Pt plane, since the related carbonyl arrangement Rh₃(CO)₃(μ-CO)₃ in [Rh₇(CO)₁₆]³⁻¹⁴ and [NiRh₆(CO)₁₆]²⁻¹⁵ exhibits CO_t ↔ μ-CO because, in these cases, the carbonyls are not coplanar with the Rh₃ triangle. The nonfluxionality of the Pt-CO group probably arises because of the greater Pt-CO bond strength and the particular geometry around Pt (vide infra).

At room temperature, the ¹⁹⁵Pt NMR spectrum is a well resolved triplet of triplets ($\delta(^{195}\text{Pt}) = 255.6$, ¹J(Pt-Rh_{ap}) = 54.9 Hz, ¹J(Pt-Rh_{eq}) = 68.6 Hz) and the direct ¹⁰³Rh spectrum showed two equally intense resonances (with associated ¹⁹⁵Pt satellites) at -257 and -991 ppm due to Rh_{eq} and Rh_{ap}, respectively. The positions of the rhodium resonances are in the same region as found for Rh_{eq} and Rh_{ap} in the related compounds [Rh₅(CO)₁₅]⁻ and [FeRh₄(CO)₁₅]²⁻¹⁶.

(c) [PtRh₄(CO)₁₂]²⁻. The 90-MHz ¹³C NMR spectrum of this anion (Figure 6) has been completely assigned by ¹³C-¹⁰³Rh and direct ¹⁰³Rh NMR measurements (Table III) and is completely in accord with the solid-state structure, which is also shown schematically in Figure 6.¹² The two distinct resonances labeled 4 and 4' (which may be interchanged) are also in keeping with the nonequivalence of these two carbonyls in the crystal structure. At -90 °C, there are three rhodium

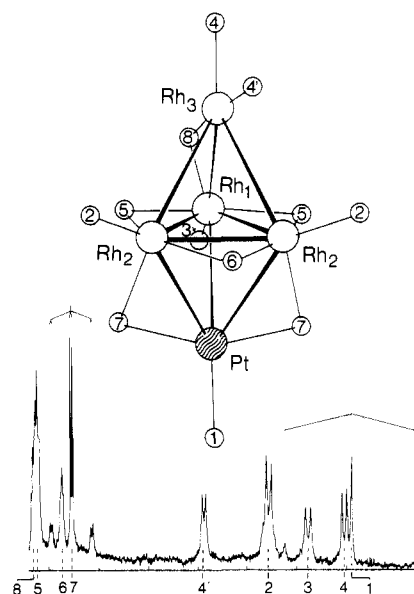


Figure 6. Top: Schematic representation of the structure of $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$. Bottom: 90-MHz ¹³C NMR spectrum of $[\text{N-}i\text{-Bu}_4]_2[\text{PtRh}_4(\text{CO})_{12}]$ in THF- d_8 at -100 °C.

resonances at +233, -432, and -475 ppm¹³ in the ratio 1:1:2 due to Rh¹, Rh³, and Rh², respectively; surprisingly only Rh¹ shows coupling to platinum (¹J(Rh¹-Pt) = 44 Hz). We have no good explanation for ¹J(Rh^{2,3}-Pt) not being observed, but it is perhaps significant that the observation of ¹J(Rh¹-Pt) involves the non-carbonyl-bridged edge and this direct interaction would reasonably be expected to be stronger than the Rh(μ-CO)Pt interactions. At higher temperatures, carbonyl exchange occurs, which results in Rh¹ and Rh² eventually becoming equivalent. However, at -55 °C the carbonyls are obviously at some intermediate rate of exchange since the direct ¹⁰³Rh NMR spectrum shows only a single sharp resonance at -435 ppm due to Rh³. This is confirmed by measuring variable-temperature ¹³C NMR spectra. At -30 °C, two broad peaks are observed at 249.7 and 216.9 ppm in the ratio ca. 3:9, which may be attributed to C⁵O/C⁶O (mean 250.6 ppm) and the remaining CO's (mean 216.7 ppm), respectively. The nonfluxionality of the μ-CO's in the equatorial plane is again similar to the behavior found for [PtRh₄(CO)₁₄]²⁻, but the involvement of the Pt-CO is different. However, [PtRh₄(CO)₁₂]²⁻ is clearly more fluxional than [PtRh₄(CO)₁₄]²⁻ since at room temperature the ¹³C NMR consists of a broad but clearly resolved 1:4:1 resonance at 225.7 ppm, J(Pt-CO) = ca. 380 Hz; the position of this resonance is also in good agreement with the calculated $\delta(\text{CO})_{\text{mean}}$, 225.2. The platinum resonance does not show any dramatic shift with

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temperature (−98 °C, +386 ppm; +25 °C, +421 ppm), and it therefore seems unlikely that the metal skeleton rearranges in solution at room temperature in the absence of CO.

8. Concluding Remarks. The equilibrium (4) between $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ and $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$ is the first example of a facile interconversion between two trigonal-bipyramidal clusters with 76 and 72 CVE's (cluster valence electrons), respectively. The fact that pentanuclear clusters, with such a geometry, can occur with 76 or 72 CVE's has been rationalized with semiempirical extended-Hückel MO calculations,¹⁷ but it remains difficult to account for the site occupancy of platinum in these two different clusters.

Over the last few years several trigonal-bipyramidal clusters have been characterized, but they mostly have 76 CVE's, except for a few osmium compounds such as $\text{Os}_5(\text{CO})_{16}$ ¹⁸ and $[\text{HOs}_5(\text{CO})_{15}]^-$,¹⁹ which have 72 CVE's. However, these osmium compounds seem reluctant to coordinate two additional CO's to give the 76-CVE clusters and only react with CO under forcing conditions, which result in opening of the cluster to give $\text{Os}_5(\text{CO})_{19}$ ²⁰ with a "bow-tie" structure. Moreover, all other known 76-CVE species, on loss of CO, generally rearrange to higher nuclearity clusters.^{5,21}

Experimental Section

All the reactions and subsequent manipulations were carried out under nitrogen or carbon monoxide atmosphere in carefully purified solvents. Na_2PtCl_6 was recrystallized and used both in the hexahydrated form and in the anhydrous form obtained by vacuum drying at 100 °C; $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ was used as commercially available with ca. 40% Rh.

¹³C-enriched samples (ca. 20–30%) were obtained by direct exchange at room temperature with 90% ¹³CO, using standard vacuum-line techniques, on various salts of $[\text{PtRh}_5(\text{CO})_{15}]^-$ and $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$; $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$ was obtained from the latter by vacuum removal of CO.

¹³C, ¹³C(¹⁰³Rh), ¹⁰³Rh, and ¹⁹⁵Pt NMR measurements were carried out as described previously,^{22–25} under ca. 1 atm pressure of ¹³CO for $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ and under N₂ for the other samples.

Infrared spectra were recorded on Perkin-Elmer 457 and 297 grating spectrophotometers and on a Nicolet MX-1 FT IR instrument with subtraction of the solvent, using 0.1-mm calcium fluoride cells previously purged with nitrogen or carbon monoxide.

1. Preparation of $[\text{PtRh}_5(\text{CO})_{15}]^-$ by Reductive Carbonylation. $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (39% Rh; 2.500 g, 9.475 mmol) and anhydrous Na_2PtCl_6 (0.859 g, 1.892 mmol) were placed in a two-necked 500-mL round-bottomed flask equipped with an inlet stopcock, a stopper, and a Teflon-covered stirring magnetic bar; methanol (60 mL) was then added and the resulting solution, with some suspended material, was briefly evacuated and submitted to approximately 1 atm CO through a mercury valve placed before the inlet in such a way as to allow accumulation of the CO₂ evolved during the reaction. After about 10 min, when saturation of the solution with CO was complete, anhydrous Na_2CO_3 (4.0 g, 37.74 mmol) was added and the mixture stirred vigorously. The maximum CO absorption was observed within the first 4 or 5 h, and special attention had to be paid in order to avoid a decrease of the pressure. The reduction slowed down as the medium became progressively buffered, and in about 18–24 h a brown solution was obtained with a white precipitate, primarily of NaCl and NaHCO₃. The solution was filtered (through a medium-porosity glass frit)

under CO, and the precipitate was washed with 10 mL of methanol to recover most of the product.

(a) Recovery of the Sodium Salt $\text{Na}[\text{PtRh}_5(\text{CO})_{15}]$. The methanolic solution of $\text{Na}[\text{PtRh}_5(\text{CO})_{15}]$, obtained according to the procedure above described, was checked by IR to confirm the presence of CO₂ (band at 2330 cm^{−1}), which assures no residual alkalinity to be present (in cases where absent, CO₂ was bubbled in or a small piece of solid CO₂ was added), and then evaporated in vacuum without any heating. The solid obtained was treated with THF (20 mL), and the resulting solution was separated from a light-brown insoluble residue by filtration under N₂; this precipitate, prior to discharge, was washed with THF (2 × 5 mL), and the washings were collected together with the main solution. Evaporation under vacuum gave the product as a light brown, extremely air-sensitive powder of good purity, according to IR, which made it a suitable starting material for most reactions, without further purification; yield 1.9 g (87%).

(b) Metathesis of $\text{Na}[\text{PtRh}_5(\text{CO})_{15}]$ with Bulky Cations. Salts of several bulky cations were obtained by metathesis performed directly on the filtered methanolic solution obtained as previously described; best results were obtained by addition of methanolic solutions containing a 5–10-fold excess of $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Br}$ or $[\text{PPN}]\text{Cl}$ and water to complete the precipitation. The product, as brown flakes, was recovered by filtration under N₂ carefully washed with water (5 × 10 mL) and 2-propanol (2 × 10 mL), vacuum-dried and stored under nitrogen. Purification was made by extraction with a 1:1 mixture of THF/*n*-pentane (or *n*-heptane) followed by further addition of *n*-pentane (or *n*-heptane). With the slow-diffusion technique the PPN derivative afforded black crystals suitable for X-ray diffraction studies.²

Anal. Found (calcd) for the $[\text{N}(\text{C}_2\text{H}_5)_4][\text{PtRh}_5(\text{CO})_{15}]$ salt: $[\text{N}(\text{C}_2\text{H}_5)_4]^+$ (gravimetric), 10.13 (10.33); Pt, 15.87 (15.48); Rh, 41.39 (40.83); CO (gas volumetric), 33.67 (33.34).

2. Preparation of $[\text{PtRh}_5(\text{CO})_{15}]^-$ by Reaction of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ and $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$. A solution of $[\text{N}-n\text{-Bu}_4]_2[\text{Rh}_{12}(\text{CO})_{30}]$ (0.190 g, 0.0742 mmol in 10 mL of THF) was treated with $[\text{N}-n\text{-Bu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ (10 mL of a THF solution 1.49×10^{-3} M) under N₂. The resulting grayish solution was divided in two portions, one being submitted to CO. This same portion slowly turned brown and gave IR evidence after 17 h of $[\text{PtRh}_5(\text{CO})_{15}]^-$ together with some $[\text{Rh}_5(\text{CO})_{15}]^-$; within a few days the mixed anion appeared almost pure. In contrast the portion left under nitrogen gave no evidence of reaction after several days.

3. Reaction of $\text{Na}[\text{PtRh}_5(\text{CO})_{15}]$ with Aqueous HCl. $\text{Na}[\text{PtRh}_5(\text{CO})_{15}]$ (0.489 g, 0.42 mmol) was dissolved in water (30 mL), and concentrated aqueous HCl (4–5 mL) was added dropwise with stirring; the precipitated brown flakes were centrifuged, separated from the mother liquor, washed with dilute HCl (1:10), and recentrifuged to give a colorless washing. The resulting vacuum-dried product dissolved only sparingly in CH₂Cl₂ and toluene. IR absorptions in CH₂Cl₂: 2065 s, 2035 m, and 1810 ms cm^{−1}.

4. Synthesis of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$. $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$ (40% Rh; 1.500 g, 5.83 mmol) and anhydrous Na_2PtCl_6 (0.659 g, 1.45 mmol) were placed in a two-necked 500-mL round-bottomed flask equipped with an inlet stopcock, a stopper, and a Teflon-covered magnetic stirring bar; methanol (50 mL) was then added, and the resulting solution with some suspended material was briefly evacuated and submitted to CO through a mercury valve maintaining a slightly positive pressure. After about 10 min, which was required to saturate the solution with CO, NaOH (0.87 M in methanol, 46 mL, 40 mmol) was added and the mixture was stirred vigorously. The maximum CO absorption was observed within the first 2 or 3 h, and special attention had to be paid in order to avoid a decrease of the CO pressure. In about 18 h an orange-yellow solution was obtained with a precipitate, primarily of NaCl and NaHCO₃. The solution was filtered (through a medium-porosity glass frit) under CO, and the precipitate was washed with 10 mL of methanol to recover most of the product. The anion was precipitated by addition of $[\text{PPN}]\text{Cl}$ (3 g in 7 mL of methanol); the precipitate, as golden yellow flakes or microcrystals, was separated from the mother liquor by filtration under CO and washed carefully with 2-propanol (10 mL), water (5 × 10 mL), and again 2-propanol (2 × 10 mL). Drying was performed briefly under vacuum, and the product was stored under CO; yield 1.6 g (53%).

The product has been obtained also as salts of several other cations such as $[\text{N}-n\text{-Bu}_4]^+$, $[\text{NEt}_4]^+$, $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$, and $[\text{PPH}_4]^+$. The procedure is the same, and precipitation occurs on addition of an excess of the chosen cation and, if necessary, water to complete the recovery. The products obtained are generally of good purity, as can be easily

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checked by IR and the color, which should be golden yellow or orange-yellow.

When the above reaction is carried out on a larger scale (6 g of $\text{RhCl}_3 \cdot x\text{H}_2\text{O}$), the best reaction is found to occur by slow addition of the NaOH solution (over ca. 2 h); this avoids a fast reduction and formation of brown insoluble products. Recrystallization to obtain high-purity compounds or a large crystalline specimen is performed by slow diffusion of 2-propanol (saturated with CO) into THF or acetone solutions, under a CO atmosphere.

Anal. Found (calcd) for the $[\text{N}(\text{C}_2\text{H}_5)_4]_2[\text{PtRh}_4(\text{CO})_{14}]$ salt: C, 28.58 (28.61); H, 3.25 (3.20); N, 2.22 (2.22); Pt, 14.70 (15.49); Rh, 34.26 (32.68).

5. Synthesis of $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$. In a typical preparation, $[\text{PPN}]_2[\text{PtRh}_4(\text{CO})_{14}]$ (0.280 g, 0.135 mmol) was dissolved in THF (15 mL) under a nitrogen atmosphere. The solution was slowly evaporated under vacuum, and the reddish brown solid obtained was redissolved in THF (15 mL); and IR spectrum revealed complete conversion to $[\text{PPN}]_2[\text{PtRh}_4(\text{CO})_{12}]$. Recovery was accomplished by addition of 2-propanol (30 mL); the microcrystalline precipitate was filtered, washed with 2-propanol (5 + 5 mL), vacuum-dried, and stored under nitrogen; yield 0.250 g (92%). The same procedure can be used to obtain any other salt using the corresponding salt of the parent compound. When larger amounts of products are worked up, more than one cycle of evaporation and redissolution may be necessary; in any case purity should be checked by IR. Recrystallization from acetone/2-propanol using the slow-diffusion technique gives good crystals of the product.

Gas Volumetric Analysis of Evolved CO. A sample of $[\text{PPN}]_2[\text{PtRh}_4(\text{CO})_{14}]$ (0.8502 g, 0.4095 mmol) was dissolved under vacuum in THF. The evolved CO (reduced to STP conditions) was 0.7875 mL, corresponding to 1.923 mol/mol of starting material.

6. Reaction of $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$ with CO. A THF or acetone solution of any salt of $[\text{PtRh}_4(\text{CO})_{12}]^{2-}$ prepared under nitrogen is briefly

evacuated and submitted to 1 atm CO; within minutes the color turns yellow from the original reddish brown and the IR spectrum taken under CO shows complete conversion to $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$.

7. Reaction of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ with $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2]^+$. $[\text{NEt}_4]_2[\text{PtRh}_4(\text{CO})_{14}]$ (0.0465 g, 0.037 mmol) was dissolved in acetonitrile under CO. Addition of $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]$ (2 mL of a 0.0185 M solution in acetonitrile) gave immediate reaction, yielding a brown solution of $[\text{NEt}_4][\text{PtRh}_5(\text{CO})_{15}]$ (IR bands at 2035 s, 2004 m, and 1775 cm^{-1}).

8. Reaction of $[\text{PtRh}_4(\text{CO})_{14}]^{2-}$ with $\text{Rh}_6(\text{CO})_{16}$. Finely powdered $\text{Rh}_6(\text{CO})_{16}$ (0.051 g, 0.048 mmol) was reacted under CO with $[\text{PPN}]_2[\text{PtRh}_4(\text{CO})_{14}]$ (4.8 mL of a 0.01 M THF solution). After 1 h of stirring, a dark red solution was obtained, which showed the characteristic IR bands of $[\text{Rh}_5(\text{CO})_{15}]^-$ (2038 s, 2004 vs, 1868 m, 1838 ms, and 1785 cm^{-1}) superimposed on those of $[\text{PtRh}_5(\text{CO})_{15}]^-$ (2035 s, 2004 m, and 1785 cm^{-1}).

Acknowledgment. We acknowledge the support of the National Research Council of Italy (CNR), SERC for a fellowship (to R.D.) and for high-field NMR facilities, and Prof. G. Longoni (Università di Milano) for the help in the identification of the platinum carbonyl species.

Registry No. $\text{Na}[\text{PtRh}_5(\text{CO})_{15}]$, 67954-67-0; $[\text{NEt}_4][\text{PtRh}_5(\text{CO})_{15}]$, 68034-57-1; $\text{PPN}[\text{PtRh}_5(\text{CO})_{15}]$, 68034-56-0; $\text{Na}_2[\text{PtRh}_4(\text{CO})_{14}]$, 91238-53-8; $[\text{PPN}]_2[\text{PtRh}_4(\text{CO})_{14}]$, 78179-93-8; $[\text{N}-n\text{-Bu}_4]_2[\text{PtRh}_4(\text{CO})_{14}]$, 91238-54-9; $[\text{NEt}_3-n\text{-Pr}]_2[\text{PtRh}_4(\text{CO})_{14}]$, 91238-55-0; $[\text{PPh}_4]_2[\text{PtRh}_4(\text{CO})_{14}]$, 91265-29-1; $[\text{NEt}_4]_2[\text{PtRh}_4(\text{CO})_{14}]$, 91238-57-2; $[\text{N}-n\text{-Bu}_4]_2[\text{PtRh}_4(\text{CO})_{12}]$, 91238-56-1; $[\text{PPN}]_2[\text{PtRh}_4(\text{CO})_{12}]$, 77906-02-6; Na_2PtCl_6 , 16923-58-3; $[\text{N}-n\text{-Bu}_4]_2[\text{Rh}_{12}(\text{CO})_{30}]$, 12576-05-5; $[\text{N}-n\text{-Bu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$, 61084-51-3; $[\text{Rh}(\text{CO})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]$, 53513-97-6; $\text{Rh}_6(\text{CO})_{16}$, 28407-51-4; $[\text{Rh}_5(\text{CO})_{15}]^-$, 72826-87-0; Rh, 7440-16-6; Pt, 7440-06-4.

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Synthesis of $\text{M}_2\text{Pt}(\text{CO})_{12}$ ($\text{M} = \text{Re}, \text{Mn}$). Crystal Structure of $\text{Re}_2\text{Pt}(\text{CO})_{12}$

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Received November 3, 1983

The heterobimetallic carbonyl compounds $\text{M}_2\text{Pt}(\text{CO})_{12}$ ($\text{M} = \text{Re}, \text{Mn}$) have been synthesized in high yield from the reaction of $\text{Me}_2\text{Pt}(\text{COD})$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) with excess $\text{HM}(\text{CO})_5$ ($\text{M} = \text{Re}, \text{Mn}$) in the presence of CO at room temperature. The concomitant formation of $\text{M}_2(\text{CO})_{10}$ is suggested as evidence of a radical pathway for this reaction. The molecular structure of $\text{Re}_2\text{Pt}(\text{CO})_{12}$ is reported and compared to the structure of $\text{Re}_2(\text{CO})_{10}$. Crystals of $\text{Re}_2\text{Pt}(\text{CO})_{12}$ form in the triclinic space group $P\bar{1}$ with $a = 7.225$ (2) Å, $b = 10.116$ (2) Å, $c = 6.503$ (2) Å, $\alpha = 94.57$ (2)°, $\beta = 91.86$ (2)°, $\gamma = 71.59$ (2)°, $V = 449.5$ (2) Å³, and $\rho(\text{calcd}) = 3.338$ g cm^{-3} , for mol wt 903.61 and $Z = 1$. The structure can best be described as a platinum atom in a square-planar environment, bound to two carbonyl ligands and two $\text{Re}(\text{CO})_5$ moieties in the trans configuration. Anisotropic refinement of all atoms has resulted in final discrepancy factors of $R = 0.030$ and $R_w = 0.038$ for 1094 observed reflections. The observed Pt-Re bond distance is 2.8309 (5) Å.

Introduction

As part of a program to evaluate oxide-supported heterobimetallic compounds as heterogeneous catalysts, we have sought high-yield pathways to new mixed-metal compounds that contain catalytically important metals.¹ One of the most important commercial bimetallic catalysts is alumina-supported platinum-rhenium, which is used in the catalytic reforming of petroleum naphthas.² To date, however, only a

few bimetallic compounds of platinum-rhenium have been reported,³ and all of them contain phosphine ligands. This is an undesirable feature for a catalyst precursor, in that supported metal particles generated from such compounds may be poisoned by phosphorus. The preparation of platinum-rhenium bimetallic compounds that contain easily removable ligands is therefore a desirable goal.

We have previously shown that mixed-metal clusters could be prepared by the addition of metal hydride complexes to

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